(12) INTERNATIONAL APPLICATION PUBLISHED ACCORDING TO THE AGREEMENT ON INTERNATIONAL COOPERATION IN PATENT MATTERS

(19) World Organization for Intellectual Property International Office [Logo] [barcode]

(43) International Publication Date April 19, 2001 (4/19/2001)

PCT

(10) International Publication Number **WO 01/27986 A1**

(51) International Patent Classification[7]: H01L 21/306, B08B 3/00, G03F 7/42

(21) International File Number: PCT/EP00/10055

(22) International Filing Date: October 12, 2000 (10/12/2000)

(25) Language of Submission: German

(26) Language of Publication: German

(30) Information on Priority: 199 49 315.4 October 13, 1999 (10/13/1999) DE

(71) Applicant *(for all covered countries except US)*: **GEBRÜDER DECKER GMBH & CO. KG** [DE/DE]; Am Goldhammer 13, 90491 Nuremberg (Germany)

(72) Inventor; and

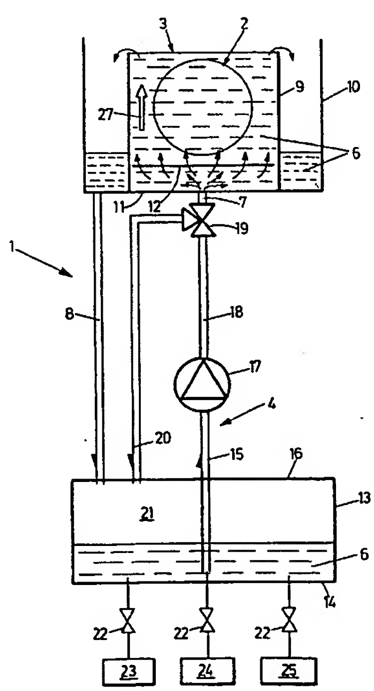
(75) Inventor/Applicant *(only for US)*: **SCHWARZ, Reinhard** [DE/DE]; Alemannenstrasse 7, 92224 Amberg (Germany). **SEEBERGER, Jürgen** [DE/DE]; Neustifterstrasse 37c, 94036 Passau (Germany). **SCHNYDER, Ulrich** [DE/CH]; Falkenriedweg 55, CH-3032 Hinterkappen (Switzerland).

(74) Attorneys: **RAU, Albrecht,** etc.; Königstrasse 2, 90402 Nuremberg (Germany).

(81) Countries Covered *(national)*: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,

[continued on the next page]

(54) Title: METHOD AND DEVICE FOR TREATING SURFACES OF OBJECTS



(57) Abstract: The invention relates to a method and device for treating the surfaces of objects, comprising the following steps: provision of a treatment installation which comprises at least one treatment chamber having at least one object disposed therein, said object having a surface to be treated; a foam-generating unit in order to generate a foam which reacts with the surface to be treated, a foam-feeding unit connecting said treatment chamber to said foam-generating unit in order to feed the foam into the at least one treatment chamber and a foam extraction unit connected to the at least one treatment chamber in order to evacuate said foam; generation of the foam by blowing a gas into a liquid containing at least one surfactant, whereby the gas and/or the liquid react with the surface to be treated; introduction of the foam to the treatment chamber of the foam-feeding unit; retention of the foam into the treatment chamber for a pre-defined period of time; evacuation of the foam through the foam extraction unit.

DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(81) **Countries Covered** ***(regional)*****:** ARIPO Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), European Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Patent (AT, BE, CH, CY, DE, DK, ES, FL, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
- *With International Search Report*

For an explanation of the two-letter codes and the other abbreviations, reference is made to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of every regular issued of the PCT Gazette.

METHOD AND DEVICE FOR TREATING SURFACES OF OBJECTS

The invention concerns a method and device for treating surfaces of objects, especially silicon wafers.

From EP 0 625 795 A1, a method is known for the wet-chemical treatment of silicon wafers, in which the wafers to be treated are placed into a processing basin through which, where possible, an aqueous solution of the chemical substances that are necessary for the surface treatment of the silicon wafers flows from below in a laminar fashion. The treatment liquid then flows over the upper rim of the process basin into a catch basin where it is either discarded or re-used. The racks bearing the silicon wafers to be treated cause turbulence and dead spots in the process basin, as a result of which the laminar flow cannot be maintained. The reactions of the surfaces of the silicon wafers with the liquid are diffusion controlled, that is, they depend upon the diffusion of the educts to the surface and the diffusion of the products away from the surfaces. This diffusion behavior is affected by the lack of homogeneity of the flow of the liquid used, resulting in wide variations with respect to the intended treatment on the surface of the silicon wafers treated. If the chemical reactions are strongly exothermic, such as, for example, etching silicon using a mixture of hydrofluoric acid and nitric acid, then the currents caused by

the heat developed are overlaid with the turbulence described above, so that the result is even worse.

A method and device for the etching of semiconductor wafers is known from EP 0 673 545 B1. The foam is produced from an etching liquid with a surfactant and an inner gas. In order to produce the foam, an etching liquid is placed under pressure with a circulating pump and inert gas is injected into the liquid and mixed with it in a static mixer. After passing through valves, the liquid is decompressed so that it foams. As a result, only a small part of the gas injected into the foam so formed can be bound, so that the method is not suitable for the use of reactive gases. At the same time, circulation is not possible; stable balance conditions are therefore not created. As a result, the primary generated spherical foam ages uncontrolled to a polyhedral foam, then finally disintegrates completely, since no energy is added to the metastable system. A stabilization of the foam can be achieved only through a heavy use of surfactants or other boundary surface active substances. In high concentrations, the boundary surface active substances can be adsorbed on the surface of the parts to be treated and cause inhibition, so that the result of the treatment is affected.

The problem to be solved by the invention is to provide a method and a device for the surface treatment of objects, which assures a surface treatment that is as even as possible. The problem is solved by the characteristics of the independent Claims 1 and 10. The core of the invention consists of using a liquid that contains a surfactant and a gas

in order to produce foam, which is used for the surface treatment, where either the liquid and/or the gas reacts with the surface in order to treat it.

Further advantageous embodiments of the invention are shown in the subsidiary claims.

Additional characteristics and details of the invention are shown in the description of two sample embodiments using the drawing. The following are shown

Fig. 1 the schematic structure of a treatment installation with a treatment chamber

Fig. 2 a schematic cross-section representation of the treatment chamber according to Fig. 1 with partial expansion of a section, and

Fig. 3 a schematic representation of the reaction kinetics of the method according to a second embodiment.

A treatment installation 1 for the surface treatment of objects in the form of silicon wafers 2 includes a treatment chamber 3, in which the silicon wafers 2 are placed. Further, a foam-generating unit 4 is provided to generate a foam 6 which reacts with the surface 5 of the silicon wafers 2 for the treatment. The foam-generating unit 4 is connected by means of a foam-feed

pipe 7 to feed the foam into the treatment chamber 3. The treatment chamber 3 is connected through a foam exhaust pipe 8 to the foam-generating unit 4 to remove the foam 6 to the foam-generating unit 4.

The treatment chamber 3 features an open overflow process basin 9, which is surrounded by an annular catch basin 10. An opening is provided in the floor 11, in the area of which the foam feed pipe 7 opens into the process basin 9. In the area of the floor 11, there is provided in the process basin 9 a horizontally oriented distribution plate 12 with numerous holes that is braced opposite the floor 11, through which the foam 6 brought in from the foam feed pipe 7 flows from the bottom upward in a flow which is as laminar as possible through the process basin 9. The silicon wafers 12 *[sic]* placed in the process basin 9 are arranged in standard racks. It is possible to move the silicon wafers 12 *[sic]* in the process basin 9 in order to homogenize the surface treatment, especially to rotate them in the plane formed by the wafer 2. The outflow pipe 8 is connected to it at a floor opening of the catch basin 10.

The foam-generating unit 4 features a mixing tank 13. In this tank, in the vicinity of the floor 14 of the tank 13, there is placed a suction pipe 15 open at the bottom, which passes through the cover plate 16 of the tank 13 and is connected to a pump 17. From the pump 17 a pipe 18 connected to it leads to a three-way valve 19, one output of which is connected to the feed pipe 7. A further output of the valve 19 is connected to a circulating pipe 20, which opens into the internal space 21 of the tank 13. The internal space 21 is

connected through cut-off valves 22 to each storage tank 23, 24, 25 to supply a liquid, a gas or a surfactant, as the case may be. The supply of the gas from the storage tank 24 is done immediately below the suction pipe 15, in order to increase foam formation. It is alternatively possible to arrange the storage tank 24 for the gas in such a manner that the gas is fed into the suction pipe 15 between the mixing tank 13 and the pump 17. As a further alternative, it is possible to feed the gas into the pipe 18 between the pump 17 and the valve 19, where, in this case, a static mixer is placed in the pipe 18, after it in the direction toward the valve 19.

In the following, the general function of the treatment installation will be described, making reference to a first sample embodiment. This regards the treatment of a silicon wafer 2 with a photosensitive coating. From the tank 23, pure water is introduced into the internal space 21. From the tank 25, a surfactant is added in a concentration of 10^{-6} to 10%, especially 10^{-4} to 10^{-2} %. The surfactant can be a commercial surfactant such as, for example, nonylphenolethoxylate, alkylbenzolsulfonate, alkansulfonate, fatty alcohol sulfate or laurylsulfate. From the tank 24, ozone gas (O_3) is blown into the water-surfactant mix, so that the foam 6 is created. By circulating the foam 6 through the suction pipe 5, the pump 17, the valve 19 and the circulating pipe 20, the foam formation is intensified. A foam similar to whipped cream results. Subsequently, the prepared foam 6 is introduced into the process basin 9 through the feed pipe 7, through which it flows from bottom to top in as laminar a fashion as possible. The foam passes the surface 5 of the silicon wafer 2 with the photosensitive coating. The ozone reacts with the photosensitive coating. In contrast to the

method described in the introduction, in which ozone gas is fed to the surface 5 in a liquid, in the boundary area at surface 5, no diffusion layers which are dependent on the local flow conditions are formed. The numerous fine gas bubbles 26 of the foam 6, which are represented magnified in Fig. 2, contain ozone. The ozone remains in the gas bubbles and reacts as undissolved ozone gas with the surface 5 of the silicon wafer 2 when the gas bubble comes in contact with it. The reactants, that is to say, the products and educts of the reaction of the photosensitive coating with the ozone, attach to the surfaces of the gas bubbles 26, as shown in Fig. 3, for a second sample embodiment. Through the rotation of the gas bubbles 26 and the movement of the gas bubbles 26 relative to each other, the reactants are transported further from gas bubble 26 to gas bubble 26. The transport of the reactants to and from the surface 5 therefore occurs substantially independently of the flow of the foam 6 along the direction of flow 27. The surface homogeneity obtained through foam treatment exceeds previously known liquid-based methods by a high multiple. After the foam 6 has passed the silicon wafer 2, it flows over the upper edge of the process basin 9 and is caught in the catch basin 10. From there, the foam 6 is again brought by the extraction pipe 8 to the tank 13 for re-use. It is, of course, also possible to discard foam 6 that has been used once and contaminated. Furthermore, it is possible to carry out multiple different treatments in sequence in a process basin 9. In this case, multiple foam-generating units 4 would be connected to the process basin 9. It is also possible, in order to remove polymers from the surface 5 of the silicon wafer 2 without photosensitive coating, to use ammoniac water (NH_4OH) as a liquid, to

which surfactants are added. In this case as well, ozone is used as a reactive gas. In order to clean the surface of the silicon wafer 2 of organic substances, ammoniac water with surfactants is used, into which ozone is blown as a reactant gas to form foam. For the cleaning of metal particles, hydrogen chloride (HCl) and surfactant-converted water is used, into which ozone is blown as a reactive gas to form the foam.

In the following, details of the process carried out in the first embodiment will be explained. The forced circulation of the foam is of central importance in the installation 1, which, for this purpose, includes a forced-circulation device. This consists of a forced-circulation device including the pump 17, the pipe 18, the valve 19, the circulation pipe 20, the mixing tank 13 as well as the suction pipe 15. This forced-circulation device serves to force the circulation of foam before it is fed to the process basin 9. A second forced-circulation device includes the pump 17, the pipe 18, the valve 19, the pipe 7, the process basin 7, the catch basin 10, the foam-extraction pipe 8, the mixing tank 13 as well as the suction pipe 15. In the case of this forced circulation, the foam is fed into the process basin 9, reacts there with the silicon wafers 2 and is then returned to the mixing tank 13. The forced circulation of the foam generated makes possible the most effective use of the gas employed, especially ozone. As a result of forced circulation, the used or decayed ozone can be continually replenished, so that the concentration of ozone in the foam bubbles reaches a condition of equilibrium. If, as according to EP 0 673 545 B1, the reaction gas is blown in only once, the concentration of the reactive

gas in the gas bubbles cannot be increased, but rather it remains in each case at the initial concentration of the gas used. In case of a gas that decays, such as, for example, ozone, the concentration of the gas in the gas bubbles is constantly decreasing. Furthermore, according to the state of technology, the concentration of the gas cannot be adjusted to reproducible values, since the system is far from equilibrium. Through forced circulation of the foam, stable equilibrium conditions can be obtained and the use and decomposition of the gas can be compensated for. The consistency of the foam generated can be adapted to the conditions necessary in each case. Especially the following parameters can be changed: the type of liquid used, the concentration of the liquid, conduction value of the liquid, temperature of the liquid, circulation power of the pump 17, type of gas used, concentration of the gas used, speed of feeding of the gas, type of surfactant used, quantity of surfactant, time of circulation and thoroughness of mixing. By changing these parameters, the following values of the foam can be affected directly or indirectly: size of bubbles in the foam, surface tension of the foam, viscosity of the foam, number of bubbles in the foam volume, half-life of the foam, half-life of the ozone, gas concentration in the bubble, pH value of the foam. The gas bubbles in the foam have a size of $1 \mu m$ to 5 mm, preferably 50 μm to 1 mm.

Depending upon the treatment solution that is necessary for the processing of the work pieces, different surfactants are used, where shorter chain surfactants are used in strongly concentrated solutions, due to solubility. In alkaline media, anionic surfactants or non-ionogenic surfactants or even mixtures of anionic and

non-ionogenic surfactants are used, while in acid media cationic surfactants or non-ionogenic surfactants or mixtures of the two are used. Surfactants with an alkyl chain of C_6 to C_8 are designated as short-chain surfactants, where these surfactants do not represent pure materials as a result of the manufacturing process, but may obtain up to 10% of other chain lengths. These decrease the surface tension less strongly than longer chain surfactants, so that the foam is stabilized. They are better soluble than long-chain surfactants (C_{16} to C_{18}) by an order of magnitude up to a factor of 100. Preferably, alkylsulfates, substituted alkylsulfates, alkylbenzosulfonates, fatty acid salts or substituted carbonic acid salts are used as anionic surfactants, where the length of the alkyl chain can be in the range of C_4 to C_{18}, preferably from C_8 to C_{14}. At the same time, the alkyl chain of the surfactant can also be perfluoridated. Preferably alcohols, amines or alkyl phenols to which two to ten molecules of ethylene oxide or propylene oxide are added per molecule or amine oxides among the non-ionogenic surfactants are used. The length of the alkyl chain can be two to 18 C-atoms, where the preferred chain length range is in the range of 4 to 14 C-atoms. Quaternary ammonium compounds and N-containing heterocyclenes such as, for example, pyridinium, chinolinium or imidazolinium compounds that contain an alkyl chain on the quaternary N-atom, where the alkyl chain can also be perfluoridated, and where the alkyl chain has 4 to 18 C-atoms, preferably 4 to 16 c-atoms, can be used as cationic surfactants.

In the concrete example, with a total volume of 85 l of water plus 70 ml 50% hydrofluoric acid, a circulation power of 60 l/min was set. By adding ozone gas with a concentration of

$200 g/Nm^3$ with 4 l/min in the pump intake pipe, shortly before the impeller wheel, the flow-through, measured with a turbine bucket sensor, drops slightly to about 58 l/min, as a result of the blowing of the intake air. By adding a surfactant (TEXAPON-ALS 25 ml), the throughput drops slowly but constantly to an equilibrium of about 35 l/min. Through further circulation with constant addition of ozone, but without supplementing the surfactant, the flow-through again rises slowly, which allows the conclusion that the surfactant is used up. Thus, a surfactant resistant to chemicals must be used or, if necessary, additional surfactant must be added.

By establishing foam circulation, the foam can be kept in the preferred form of a spherical foam. The necessary consistency of the foam can be reached and maintained by adjusting the easily controllable above-mentioned parameters so that stable process conditions, such as, for example, a consistent removal, can be obtained. As a result, it is possible to use the device for various tasks. Through the forced circulation of the foam, it is possible when reactive gases are used, to supply constantly the educts necessary for the reaction and to remove the reaction products from the surface of the work pieces to be processed, where even gases that decay relatively rapidly can be used, such as ozone, as a result of their high reactivity. In this manner, even with these materials, high process security can be achieved in a manufacturing process and consistent rates of removal can be achieved where, at the same time, the removal is done homogeneously for the entire surface.

In the following, a second embodiment of the invention will be described with reference to Fig. 3. In this case, what is involved is etching the silicon

wafer, which is represented in larger scale in Fig. 3, where the individual silicon atoms are designated with the reference figure 28. In order to generate the foam, nitric acid (HNO_3) and hydrofluoric acid (HF) are added to the internal space 21 from the tank 23. These liquids are the substances that react with the silicon surface. To generate the foam, nitrogen gas (N_2) is blown in, which behaves inertly during the reaction of the liquid with the silicon surface and serves only to generate foam. The foam 6 generated is fed through the process basin 9 and there comes in contact with the silicon wafers 2. The kinetics of the resulting reactions are shown schematically in Fig. 3. The educts, intermediate products and products of the individual reactions adhere to the surface of the gas bubbles 26 filled with nitrogen. As a result of the rotation of the gas bubbles 26, the reactants are transported to and from the silicon surface. The reactions that occur in this connection can be described by the following reaction equations:

$$
\begin{array}{lllll}
Si & + 2HNO_3 & \rightarrow & SiO_2 & + 2HNO_2 \\
 & 2HNO_2 & \rightarrow & H_2O + & NO + NO_2 \\
\underline{SiO_2} & \underline{+ \ 6\,HF} & \underline{\rightarrow} & \underline{H_2SiF_6 +} & \underline{2H_2O} \\
Si + & 2HNO_3 \ 6\,HF & \rightarrow & H_2SiF_6 + & 3\,H_2O + NO\uparrow + NO_2\uparrow
\end{array}
$$

In this case as well, the surface reactions, due to the lack of a diffusion boundary layer, are essentially independent of the flow behavior of the foam 6 in the process basin 9, so that an outstanding surface homogeneity of the silicon wafers 2 is obtained. In order to remove oxides on the surface of the silicon wafer 2, hydrofluoric acid (HF) with a surfactant can be used, into which gaseous nitrogen (N_2) as an inert gas is blown to form foam.

In order to etch aluminum conducting paths that have been applied to the silicon wafer 2 in connection with semiconductor manufacture, a mixture of phosphoric acid (H_3PO_4), nitric acid (HNO_3) and acetic acid (CH_3COOH) containing a surfactant can be used as the liquid, into which the nitrogen gas is blown in as an inert gas to generate foam. In all of the above-mentioned cases, nitrogen serves only to generate foam.

It is possible to use any other gases such as ammonia gas (NH_3), hydrogen chloride gas (HCl), hydrogen fluoride gas (HF) to create foam, which also serve for foam generation. In addition, the method described can also be used to treat completely different objects than silicon wafers. For example, sintered ceramics, coated metal surfaces, etc. come into consideration, in which an especially homogeneous and even surface treatment by chemical materials is necessary. If the material to be used in the treatment is a gas, then it can be used to form the foam. If the material used for surface treatment is a material that is soluble in any liquid, then an inert gas, such as, for example, nitrogen, or a noble gas such as, for example, argon, can be used to generate foam.

Patent Claims

1. A method for treating the surfaces of objects, comprising the following steps:
   a) provision of a treatment installation which comprises
      i. at least one treatment chamber (3) having at least one object disposed therein, said object having a surface to be treated (5);
      ii. a foam-generating unit (4) in order to generate a foam (6) which reacts with the surface to be treated (5),
      iii. a foam-feeding unit (7) connecting said treatment chamber (3) to said foam-generating unit (4) in order to feed the foam (6) into the at least one treatment chamber (3) and
      iv. a foam extraction unit (8) connected to the at least one treatment chamber (3) in order to evacuate said foam (6),
   b) generation of the foam(6) by blowing a gas into a liquid containing at least one surfactant, whereby the gas and/or the liquid react with the surface to be treated (5),
   c) introduction of the foam (6) into the treatment chamber (3) by the foam-feeding unit (7),
   d) retention of the foam (6) in the treatment chamber (3) for a predetermined period of time and

e) evacuation of the foam through the foam-extraction unit (8).

2. Method in accordance with Claim 1, characterized in that, the at least one surfactant has a concentration of 10^6 to 10%.

3. Method in accordance with Claim 1 or 2, characterized in that, the gas is a noble gas, carbon dioxide, chlorine gas, fluorine gas, air, ozone, nitrogen, ammonia, hydrogen fluoride, hydrogen chloride, di-phosphorous pentoxide, nitrogen dioxide or a mixture of these gases.

4. Method in accordance with one of the foregoing Claims, characterized in that, the liquid is pure water, ammoniated water, hydrochloric acid, hydrofluoric acid, nitric acid, phosphoric acid or acetic acid.

5. Method in accordance with one of the foregoing Claims, characterized in that, the object is a silicon wafer (2).

6. Method in accordance with Claim 5, characterized in that photosensitive coating, polymers, organic compounds, metals, silicon oxide, silicon or aluminum are removed from the surface (5).

7. Method in accordance with one of the foregoing Claims, characterized in that, the foam-generating unit (4) features a pump-driven forced circulation to increase foam formation.

8. Method in accordance with one of the foregoing Claims, characterized in that, the foam-extraction unit (8) feeds the foam (6) to the foam-generating unit (4) for re-use.

9. Method in accordance with one of the foregoing Claims, characterized in that, the foam (6) flows through the treatment chamber (3) with a speed of 0.1 to 1000 l/min.

10. A device for carrying out the method according to one of the foregoing claims, comprising:
    a) at least one treatment chamber (3) having at least one object disposed therein, said object having a surface to be treated (5);
    b) a foam-generating unit (4) in order to generate a foam (6) which reacts with the surface to be treated (5),
    c) a foam-feeding unit (7) connecting said treatment chamber (3) to said foam-generating unit (4) in order to feed the foam (6) into the at least one treatment chamber (3) and
    d) a foam extraction unit (8) connected to the at least one treatment chamber (3) in order to evacuate said foam (6).